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SINGLET→ TRIPLET TRANSITION IN PARA-CHLOROTOLUENE

J. K. ROY*

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, JADAVPUR, CALCUTTA 32

(*Received, March* **20**, 1959)

Plate IV

ABSTRACT. The luminescence spectra excited in para-chlorotoluene have been studied using monochromatic radiations of different wavelengths. It has been observed that such a radiation of wavelength as large as 3750 Å excites the luminescence bands. As the near ultraviolet absorption band due to singlet→ singlet* transition in this case is at 2760 Å it has been concluded that the observed luminescence is produced by absorption of the radiation due to the singlet → triplet transition and that the selection rule is violated in this case owing to the particular type of substitution.

INTRODUCTION

It was first observed by Sanyal (1953) while studying the Raman spectra of ortho- and para-chlorotoluene at low temperatures, that either of these two substances exhibits strong luminescence in the visible region in the solid state at −180°C. Later, Biswas (1954, 1955a, 1955b) observed that many disubstituted benzene compounds irradiated with 3650 Å group of Hg lines at −180°C give rise to similar luminescence in the visible region. It has also been observed (Sirkar and Biswas, 1956 and Biswas, 1956 a) that the intensity of this luminescence increases rapidly with lowering of temperature of the solidified mass and the relative intensities of the bands in the band system are altered considerably when the substance is dissolved in different solvents such as benzene, *n*-heptane, cyclohexane, methyl alcohol, etc. Using suitable light filters, Biswas (1956b) has also observed that the group of Hg lines at 3650Å and other lines of shorter wavelengths upto 3000Å are responsible for the production of this luminescence. The 0,0 band in the absorption spectrum due to solid *p*-chlorotoluene at −180°C had been observed by Swamy (1952) to be at 2760Å and therefore it was surprising that radiation of wavelengths much longer than 2760Å could excite the strong luminescence without absorbing light in the process of singlet-singlet* transition. The excitation of luminescence in *p*-chlorotoluene by the 3650Å group of Hg-lines indicates that the *p*-chlorotoluene molecule in the solid state at −180°C absorbs radiation of wavelengths as long as 3650Å. Such absorption could not

* Communicated by Prof. S. C. Sirkar.

be detected by Biswas (unpublished results). He, however, (Biswas 1958) observed that part of the luminescence is produced by delayed emission. Biswas did not use monochromatic radiation of different wavelengths to excite the luminescence. It was, therefore, not known whether any monochromatic radiation of wavelength longer than 3650Å could excite the luminescence. It was, therefore thought worthwhile to study the luminescence spectra of these substances using different monochromatic exciting radiations in the region from 3500Å—4000Å eliminating all radiations of shorter wavelengths in order to understand the process which gives rise to this luminescence.

EXPERIMENTAL

In order to get the monochromatic radiations of large intensity, light from a carbon arc running at 5 amps was focussed with the help of a large glass condenser on the entrance slit of a plane grating monochromator in which a large schlieren concave mirror was used both as a collimator and as the camera lens. The glass condenser cut off all wavelengths below 3000Å. Radiations of different wavelengths could be taken out from the exit slit of the monochromator by turning the plane grating about a vertical axis. The light coming out through the exit slit of the monochromator was allowed to irradiate the sample contained in a sealed tube of Pyrex glass. The tube was immersed in liquid oxygen in a Dewar vessel in order to lower the temperature of the substance. The scattered light at right angles to the incident beam was focussed on the slit of a Fuess glass spectrograph having a dispersion of about 11Å/mm in the 4046Å region and the spectrum was photographed on Ilford HP3 films. Such spectrograms were taken using exciting radiations of wavelengths 3650Å, 3750Å and 3800Å. Iron arc spectrum was superposed on each spectrogram using Hartmann diaphragm for comparison.

As the luminescence bands are broad, the widths of the slit of the spectrograph was increased to about 0.7 mm to reduce the time of exposure Even with such a wide slit the time of exposure varied from 7 hours to 14 hours. The substance was of pure quality and was distilled in vacuum to remove dissolved impurities.

RESULTS AND DISCUSSION

The three spectrograms mentioned above are reproduced in Plate IV. The positions, approximate widths and the estimated relative intensities of the luminescence bands exhibited by pure *p*-chlorotoluene in the solid state at—180°C excited by the 3650Å and 3750Å respectively are given in Table I. The relative intensities are indicated as very strong (vs), strong(s) etc. in the table. The radiation of wavelength 3800Å did not excite any luminescence.

It will be seen from figure 1 (Plate IV) that the bands excited by 3650Å radiation photo graphed with an exposure of 7 hours is many times more intense than the bands due to 3750Å although the exposure in the latter case is 11 hours.

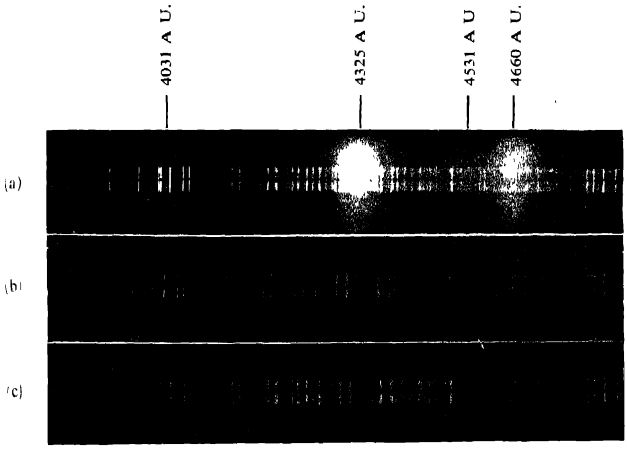

Fig 1. Luminescence spectra of *p*-chlorotoluene at −180°C
(a) Excited by 3650 A U. (b) Excited by 3750 A U (c) Excited by 3800 A U.

It is evident from these spectrograms that the radiation of wavelength as large as 3750Å excites the luminescence in this case, and therefore, the radiation

TABLE I

Luminescence spectra of *p*-chlorotoluene at −180°C

Exciting wavelength in A.U.	Wavelengths of the bands in A.U. (present author)	Wavelengths of the bands in A.U (Biswas, 1956a)	Width of the band in A U. (present author)
3650Å	4031 (S)	4038 (s)	66
	4219 (w)	4219 (m)	75
	4325 (vs)	4325 (vs)	113
	4531 (s)	4529 (s)	80
	4660 (vs)	4660 (vs)	105
	—	4807 (vw)	
	—	4900 (w)	
	—	5031 (vw)	
3750Å	4325 (s)		91
	4531 (w)		74
	4660 (s)		89
3800Å	No band		

is first absorbed in the process of singlet-triplet transition and then re-emitted. As shown by Biswas (1958) part of the luminescence consists of phosphorescence and therefore the triplet-singlet transition is responsible for the origin of this phosphorescence.

As the intensity of luminescence is fairly large the initial absorption is also large The failure in detecting this large absorption in the region from 3600Å −3800Å by Biswas is evidently due to the fact that the triplet state has a large lifetime and therefore once some molecules are excited they do not return to the ground state for sometime and the incident radiation during this time is transmitted without any further absorption.

The violation of the selection rule regarding the transition from the singlet to triplet state in this particular case seems to be due to the particular substitution in the benzene ring, because neither dichlorobenzenes nor xylenes exhibit such a strong luminescence in this region in the solid state at low temperatures. The violation of the selection rules in this case is thus definitely established by the results of the present investigation.

ACKNOWLEDGMENT

The author's thanks are due to Prof. S. C. Sirkar, D.Sc., F.N.I, for his kind interest and constant guidance during the progress of the work.

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